



Physicochemical Characteristics and Microbial Quality of an Oil Polluted Site in Gokana, Rivers State.

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ABSTRACT: Samples were collected from the soil surface area, the water surface, sub-surface sediment sand, sand from the river shore, Dead Sea food and dead mangrove vegetation leaves. Test results indicated that the Total Heterotrophic Bacteria (THB) values ranged from $(9.0 \times 10^3 - 2.6 \times 10^6)$ cfu/ml with the sample from the water surface having the highest value (2.6×10^6) cfu/ml and the least with the sample from the sub-surface (9.0×10^3) cfu/g. The Total coliforms values ranged from $(6.9 \times 10^3 - 2.3 \times 10^6)$ cfu/100g with sample from the dead vegetation leaves having the highest value (2.3×10^6) cfu/100g and the least value from the sample from mangrove substrate (6.9×10^3) cfu/100g. Among the physico-chemical parameters tested, TDS, lead, copper, chromium, cobalt, zinc, cadmium, nickel and arsenic were within acceptable limits as specified by regulatory agents. However, electrical conductivity, oil and grease, and iron were very high and above specified limits. The pH values ranged from 3.90 – 8.15 with the sample from the mangrove substrate having the highest value (8.15) and the lowest value was from the sample from the crude on water surface (3.90). The electrical conductivity values ranged from (1275 – 3565) $\mu\text{S/cm}$ with sample from crude band on soil surface having the highest value (3565) $\mu\text{S/cm}$ and the lowest value from the sample from the sub-surface sediment sand (1275) $\mu\text{S/cm}$. The oil and grease values ranged from (620 – 32040) mg/kg with sample from soil surface having the highest value (32040) mg/kg and the lowest value from the river shore sand (620) mg/kg. The high level of oil and grease contamination poses a concern. This therefore, validates the concern that releases of large quantities of oil to aquatic and terrestrial environments present a long term threat to all forms of life. @ JASEM

On land, crude oil spills have caused great negative impact on food productivity. For example, a good percentage of oil spills that occurred on the dry land between 1978 and 1979 in Nigeria, affected farmlands in which crops such as rice, maize, yams, cassava plantain were cultivated (Onyefulu and Awobajo, 1979). Crude oil affects germination and growth of some plants (Onwurah 1999a). It also affects soil fertility but the scale of impact depends on the quantity and type of oil spilled. Spilled petroleum hydrocarbons in the environment are usually drawn into the soil due to gravity until an impervious horizon is met, for example bedrock, watertight clay or an aquifer. Poor miscibility of crude oil accounts for accumulation of free oil on the surface of ground water and this may migrate laterally over a wide distance to pollute other zones very far away from the point of pollution. Industrial and municipal discharges as well as urban run-offs, atmospheric deposition and natural seeps also account for petroleum hydrocarbon pollution of the environment. It is worthy of note that groundwater is one of the many media by which human beings, plants and animals come into contact with petroleum hydrocarbon pollution. Crude oil and petroleum are complex mixtures of several polycyclic aromatic compounds and other hydrocarbons (Domask, 1984). Contamination of soil arising from spills is one of the most limiting factors to soil fertility and hence crop productivity (Onwurah et al., 2007). Report revealed

that thirteen years after the Exxon Valdez oil spill in Prince William Sound, the toxic effects are still being felt due to the remaining bulk of the less-weathered subsurface oil (Short, et al., 2002). A random sampling of underground fuel storage tanks conducted by U.S. Environmental Protection Agency (USEPA) in the United States revealed about 35% leaks in these tanks (United Press International, 1986). The major concern with crude oil spill has been its contamination of ground water, and the subsequent clean up.

Crude oil pollution of the environment may arise from oil well drilling production operations, transportation and storage in the upstream industry, and refining, transportation, and marketing in the downstream industry. It could also be from anthropogenic sources (Oberdorster and Cheek, 2000). Sources of petroleum and its products in the environment will also include accidental spills and from ruptured oil pipelines (Beller, et al., 1996). One of the major fates of spilled petroleum oil in the coastal environment is its incorporation into the sediments (Alexander and Webb, 1987). Problems associated with the study and remediation of the polluted ecosystem can be very expensive. The legal problems related to compensation in terms of assigning monetary reward may bring serious controversy. This study is therefore undertaken to determine the extent of oil pollution on a polluted site

by investigating the physicochemical characteristics and microbial qualities of some selected parameters.

MATERIALS AND METHODS

Samples for Physicochemical and Microbiological Analyses

Samples were taken at different depths and distances from crude band on muddy area, film of crude on water surface, sub-surface sediment sand, surface black mud with crude spill, sand collected on river shore, dead sea food and dead mangrove vegetation leaves.

About 1kg soil materials were collected in plastic bags and sampling protocols in line with analytical procedures as outlined in Part VII Section D of Guidelines and Standards for the Petroleum Industry were followed. One litre of effluent sample was collected and stored ice block cooler for preservation before being transferred to the laboratory for analysis (DPR, 1991; FEPA, 1991).

The need for sampling at the various points was to determine the extent of pollution in terms of percolation and dispersion plume. All the collected samples were preserved in accordance with guidelines and International Standards. All other QA/QC procedures relevant to sample collection, custody and analyses were strictly adhered to (APHA 1995; ASTM, 1979).

Due diligence were taken to prepare them for specified tests as indicated below.

pH Value Determination

The 50ml beaker was half-filled with the samples. Water was added to just sufficient depth to allow immersion of the electrode. Mixing was carried out using a gentle shaker and stirred frequently for a few minutes. Then allowed to stand for a further 15 minutes. The electrode of the meter was immersed into the slurry and waited for needle drift to cease. The pH was recorded for each sample.

Electrical Conductivity (EC) determination

A saturated paste of the crushed/ soil samples were made using distilled water. The electrical conductivity of the samples was determined electrometrically with a calibrated electrical conductivity meter.

Heavy Metals Determination

A measured quantity of the samples were transferred into a Kjeldahl flask; 20ml of concentrated nitric acid (HNO_3) was added and the sample pre-digested by heating gently for 20mins. More acid was thereafter added and digestion was continued for 30-40mins. Digestion was stopped when a clear digest was obtained. The flask was cooled and the content

transferred into a 50ml volumetric flask and made to the mark with distilled water. The resulting solution was analysed for heavy metals using the Atomic Absorption Spectrophotometer (AAS).

Oil & Grease Determination

The soil sample was mixed using a glass rod or spatula. The samples were dried in the oven at $105^\circ\text{C} \pm 2^\circ\text{C}$ for two hours (2Hrs). The dried material was disaggregated by gently crushing any lumps in a mortar. About 5.0g of the sample was weighed into a 120ml glass bottle for extraction. About 20ml of the solvent was added into the bottle and extracted in a vibrating bath for three hours, allowed to settle and filtered into a clean bottle. The concentration was determined photometrically.

Total Heterotrophic Bacteria

For Soil Samples

About 1.0g of grounded soil/sediment samples were aseptically transferred, using a flame-sterilized steel spatula, into a sterile test tube containing 9ml of the diluent. This gave 10^{-1} dilution. Subsequently, four fold (10^{-4}) serial dilutions were prepared from the 10^{-1} dilution.

For Water Samples

About 1ml of the crude/film of crude on water surface samples was aseptically transferred, using a sterilized dropper, into a sterile test tube containing 9ml of the diluent. This gave 10^{-1} dilution. Subsequently, four fold (10^{-4}) serial dilutions were prepared from the 10^{-1} dilution.

Inoculation and Enumeration of Both Water and Soil Samples

0.1ml aliquot of 10^{-4} dilution was aseptically removed with a sterile pipette and spread plated with flame sterilized glass spreader on well dried agar plates. This was incubated at $28 \pm 2^\circ\text{C}$ for 24hrs. The colonies counted were expressed as colony forming unit per gram for soil/sediment/dead sea food/dead mangrove vegetation leaves and colony forming unit for water samples.

Total Coliforms

For Soil Samples

About 1.0g of grounded soil/sediment samples were homogenized with 20ml of distilled water in 100ml volumetric flask. Then make up to the mark with distilled water. This should be done in triplicates. This gives a dilution factor of 10^2 . The diluted samples were filtered through membrane filter with the aid of vacuum pump. The filter membrane was placed in the m-HPC agar plate. This was then

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incubated using an incubator pre-set to $28 \pm 2^\circ\text{C}$ for 24hrs. Observation was made for colony development on the filter membrane. The colonies were then counted as colony forming unit per 100g.

For Water Samples

About 100ml of the crude/film of crude on water surface samples was filtered through membrane filter with the aid of vacuum pump. The filter membrane was placed in the m-HPC agar plate. This was then incubated using an incubator pre-set to $28 \pm 2^\circ\text{C}$ for 24hrs. Observation was made for colony development on the filter membrane. The colonies were then counted as colony forming unit per 100ml.

RESULTS AND DISCUSSION

Test results from samples as specified are indicated in the tables as below.

Table 1: Microbiological Quality of Crude Band on Muddy Area (Sample 1)

S/N	Parameter	Test result
1.	Total Heterotrophic Bacteria (cfu/g)	9.0×10^3
2.	Total Coliforms (cfu/100g)	8.0×10^5

Table 2: Microbiological Quality of Film of Crude on Water Surface (Sample 2)

S/N	Parameter	Test result
1.	Total Heterotrophic Bacteria (cfu/ml)	2.6×10^6
2.	Total Coliforms (cfu/100ml)	2.1×10^6

Table 3: Microbiological Quality of Sub-surface Sediment Sand, 0.5m Deep (Sample 3)

S/N	Parameter	Test result
1.	Total Heterotrophic Bacteria (cfu/g)	6.2×10^2
2.	Total Coliforms (cfu/100g)	6.0×10^5

Table 4: Microbiological Quality of Surface Black Mud with Crude Spill (Sample 4)

S/N	Parameter	Test result
1.	Total Heterotrophic Bacteria (cfu/g)	1.4×10^5
2.	Total Coliforms (cfu/100g)	2.0×10^6

Table 5: Microbiological Quality of Sand Collected on River Shore (Sample 5)

S/N	Parameter	Test result
1.	Total Heterotrophic Bacteria (cfu/g)	1.5×10^3
2.	Total Coliforms (cfu/100g)	1.4×10^5

Table 6: Microbiological Quality of Dead Sea Food, Oyster on Mangrove Substrate (Sample 6)

S/N	Parameter	Test result
1.	Total Heterotrophic Bacteria (cfu/g)	1.9×10^4
2.	Total Coliforms (cfu/100g)	6.9×10^3

Table 7: Microbiological Quality of Dead Vegetation Leaves (Sample 7)

S/N	Parameter	Test result
1.	Total Heterotrophic Bacteria (cfu/g)	1.2×10^4
2.	Total Coliforms (cfu/100g)	2.3×10^6

Table 8: Physicochemical Analysis of Crude Band on Muddy Area (Sample 1)

S/N	Parameter	Test result
1.	pH	6.70
2.	TDS (mg/l)	1758
3.	EC ($\mu\text{S}/\text{cm}$)	3565
4.	Oil and Grease (mg/l)	1956
5.	Nickel (mg/l)	<0.001
6.	Cadmium (mg/l)	<0.001
7.	Chromium (mg/l)	0.023
8.	Cobalt (mg/l)	<0.001
9.	Copper (mg/l)	0.002
10.	Lead (mg/l)	0.006
11.	Zinc (mg/l)	0.057
12.	Iron (mg/l)	12.680
13.	Arsenic (mg/l)	<0.001

Table 9: Physicochemical Analysis of Film of Crude on Water Surface (Sample 2)

S/N	Parameter	Test result
1.	pH	3.90
2.	TDS (mg/l)	1530
3.	EC ($\mu\text{S}/\text{cm}$)	3105
4.	Oil and Grease (mg/l)	1363
5.	Nickel (mg/l)	<0.001
6.	Cadmium (mg/l)	<0.001
7.	Chromium (mg/l)	0.113
8.	Cobalt (mg/l)	<0.001
9.	Copper (mg/l)	<0.001
10.	Lead (mg/l)	<0.001
11.	Zinc (mg/l)	0.139
12.	Iron (mg/l)	0.574
13.	Arsenic (mg/l)	0.001

Table 10: Physicochemical Analysis of Film of Sub-surface Sediment Sand, 0.5m Deep (Sample 3)

S/N	Parameter	Test result
1.	pH	7.39
2.	EC ($\mu\text{S}/\text{cm}$)	1275
4.	Oil and Grease (mg/kg)	4960
5.	Nickel (mg/kg)	0.001
6.	Cadmium (mg/kg)	<0.001
7.	Chromium (mg/kg)	0.002
8.	Cobalt (mg/kg)	<0.001
9.	Copper (mg/kg)	<0.001
10.	Lead (mg/kg)	0.002
11.	Zinc (mg/kg)	0.078
12.	Iron (mg/kg)	5.828
13.	Arsenic (mg/kg)	<0.001

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Table 11: Physicochemical Analysis of Film of Surface Black Mud with Crude Spill (Sample 4)

S/N	Parameter	Test result
1.	pH	7.45
2.	EC (µS/cm)	1436
4.	Oil and Grease (mg/kg)	32040
5.	Nickel (mg/kg)	0.001
6.	Cadmium (mg/kg)	<0.001
7.	Chromium (mg/kg)	<0.001
8.	Cobalt (mg/kg)	<0.001
9.	Copper (mg/kg)	<0.001
10.	Lead (mg/kg)	0.002
11.	Zinc (mg/kg)	0.078
12.	Iron (mg/kg)	18.47
13.	Arsenic (mg/kg)	<0.001

Table 12: Physicochemical Analysis of Sand Collected on River Shore (Sample 5)

S/N	Parameter	Test result
1.	pH	7.64
2.	EC (µS/cm)	1771
4.	Oil and Grease (mg/kg)	620
5.	Nickel (mg/kg)	0.002
6.	Cadmium (mg/kg)	<0.001
7.	Chromium (mg/kg)	<0.001
8.	Cobalt (mg/kg)	<0.001
9.	Copper (mg/kg)	0.001
10.	Lead (mg/kg)	<0.001
11.	Zinc (mg/kg)	0.038
12.	Iron (mg/kg)	3.237
13.	Arsenic (mg/kg)	<0.001

Table 13: Physicochemical Analysis of Dead Sea Food, Oyster on Mangrove Substrate (Sample 6)

S/N	Parameter	Test result
1.	pH	8.15
2.	EC (µS/cm)	1429
4.	Oil and Grease (mg/kg)	5360
5.	Nickel (mg/kg)	0.001
6.	Cadmium (mg/kg)	<0.001
7.	Chromium (mg/kg)	0.098
8.	Cobalt (mg/kg)	0.001
9.	Copper (mg/kg)	0.001
10.	Lead (mg/kg)	0.006
11.	Zinc (mg/kg)	0.058
12.	Iron (mg/kg)	6.038
13.	Arsenic (mg/kg)	0.75

Table 14: Physicochemical Analysis of Dead Vegetation Leaves (Sample 7)

S/N	Parameter	Test result
1.	pH	5.95
2.	EC (µS/cm)	2158
4.	Oil and Grease (mg/kg)	19260
5.	Nickel (mg/kg)	0.002
6.	Cadmium (mg/kg)	<0.001
7.	Chromium (mg/kg)	0.170
8.	Cobalt (mg/kg)	<0.001
9.	Copper (mg/kg)	<0.001
10.	Lead (mg/kg)	0.001
11.	Zinc (mg/kg)	0.071
12.	Iron (mg/kg)	3.714
13.	Arsenic (mg/kg)	0.35

Results of the different samples from the different sampling locations of the soil surface, sub-surface (0.5m) depth, water surface, river shore, mangrove substrate and dead vegetation leaves are presented in tables (1 – 14). Tables (1 – 7) are results for microbiological quality from the seven sample points while tables (8 – 14) are for physicochemical analysis respectively.

Test results indicated that Total heterotrophic bacteria for soil surface sample (table 1) was 9.10×10^3 cfu/g, 2.6×10^6 cfu/g for water surface (table 2), 6.2×10^2 cfu/g for soil sub-surface (0.5m) depth (table 3), 1.4×10^5 cfu/g for highly polluted soil surface (table 4), 1.5×10^3 cfu/g for the river shore sand (table 5), 1.9×10^4 cfu/g for mangrove substrate (table 6) and 1.2×10^4 for dead vegetation leaves (table 7). The result was higher with the sample from the water surface followed by the sample from highly polluted surface and least with the sample from the soil sub-surface (0.5m) depth. The highest number of microbial load seen with sample from water surface could be attributed to activities, nutrient and aeration at the surface that enhances microbial growth and the least number seen in the sub-surface could be attributed to anaerobic conditions and nutrient depletion that inhibits microbial growth.

The total coliforms ranged from $6.9 \times 10^3 - 2.30 \times 10^6$ cfu/100g (table 1-7). With the sample from the dead vegetation leaves giving the highest number and the least from the sample from mangrove substrate (table 6). There is a strong indication that the dead vegetation leaves provided a fertile ground for the microbes to grow while mangrove substrate lack necessary nutrients to favour the growth of the microbes.

As specified in the guidelines for Environmental officers (EHO's) limit for food materials, the total coliforms results were higher with sample from

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Oyster mangrove substrate and dead vegetation leaves.

The physicochemical results are presented in tables (8-14). Among the parameters tested, TDS, lead, copper, chromium, zinc, cobalt, cadmium, nickel and arsenic were within acceptable limit as specified by regulatory agents. However, electrical conductivity, oil and grease, iron and pH were very high and above specified limits. The pH value ranged from (3.90 – 8.15). The highest was with the sample from the mangrove substrate and lowest was from the water surface sample. The various contaminants in the water surface would have resulted to increase of the acidity level of the water body thereby lowering the pH value as seen. The electrical conductivity ranged from (1275-3565) $\mu\text{S}/\text{cm}$ with highest value seen with the sample from soil surface (table-8) and least with sample from sub-surface soil (table-10). Electrical conductivity levels are affected by geology and soils constituents (Boyd,1982). The oil and grease values ranged from (620-32040) mg/kg, with the highest value seen in the highly polluted soil surface sample (table-11) and the least in the river shore sample (table -12). The high level of contamination with oil and grease poses a great concern and long term threat to all forms of life.

Conclusion: When oil spill occurs, it poses a long term threat to all forms of life. To address this concern, immediate remediation technology should be carried out to restore affected areas to base – line level. Due diligence to be adhered to for continuous monitoring to validate the effectiveness of mitigation.

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